Comparison of methods for quantitative analysis of additives in low-density polyethylene using supercritical fluid and enhanced solvent extraction

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Abstract

On-line supercritical fluid extraction–supercritical fluid chromatography (SFE–SFC) with cryogenic trapping was used to extract and separate five additives from a low-density polyethylene (LDPE) sample. A glass tube filled with glass wool afforded excellent collection efficiency for the extracted analytes. Additive spiked sand was employed to optimize the various parameters of the on-line SFE–SFC system. Calibration curves from the spiked sand studies for on-line SFE–SFC were obtained with good linearities for quantitation. Results obtained on additives in LDPE from on-line SFE–SFC were comparable to those from off-line SFE–HPLC and off-line enhanced solvent extraction (ESE)–HPLC for all additives except Irganox 1076. However, the precision obtained with on-line SFE–SFC was lower than that from off-line SFE–HPLC and off-line ESE–HPLC due to the small sample size employed in the on-line system. Considerable clean-up of the ESE extract was required prior to chromatographic analysis. On-line SFE–SFC minimized the sample handling and eliminated the use of organic solvent. Despite the lower than expected precision, the on-line SFE–SFC method for quantitation of polymer additives appears to be reliable and robust for application in routine quality control analysis. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

As the purity and amount of additives incorporated into a polymer product affect the properties of the polymer, there is a need for reliable and rapid analytical methods to characterize the additives and to determine the amount of additive present. Traditional liquid solvent–polymer extraction methods are time-consuming and uneconomical. They involve dissolution of the polymer in a hot solvent such as toluene [1], chloroform, or decalin [2], followed by precipitation of the high molecular weight fraction with an alcohol or by cooling. Further separation of the extractables is usually required prior to analysis. Analysis by conventional GC is limited [3] because many additives are non-volatile and high molecular weight. Aluminum-clad high-temperature capillary GC columns have been used but such methods have been found to lack reproducibility [4]. Owing to the relatively high molecular weight, reactivity, polarity, thermolability, and volatility of certain additives, LC

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has been the most commonly used chromatographic technique [5–8].

Recent studies with polymer additives have shown that supercritical fluid extraction [9] (SFE) is as efficient as conventional liquid/solid extraction and less time-consuming. Supercritical fluid chromatography (SFC) techniques have also been demonstrated to be highly useful for determination of polymer additives, owing to the ability to use SFC with mass-sensitive flame ionization detection (FID). Coupling SFE to SFC is quite possible. Thus, on-line SFE–SFC for the determination of additives in polymers is believed to have considerable potential.

Ashraf-Khorassani et al. [10,11] investigated the quantitative determination of a variety of polymer additives using the technique of SFE–cryogenic trapping–SFC. A polyethylene glycol (PEG) silica-based packed column was used for SFC separation and FID was employed for detection. Cotton et al. [12] described the extraction and separation of both additives and oligomers from polypropylene (PP). Fused-silica open tubular columns were used to perform the SFC separation at 120°C with pressure programming. The use of on-line SFE–SFC was described by Hirata et al. [13] with a capillary column packed with octadecylsilica (ODS). In a further study by Daimon and Hirata [14], the use of wall coated capillaries of different film thicknesses for concentrating extracted solutes was evaluated by comparing the recoveries of C_{12} to C_{20} alkanes at room temperature. The capillary with a 0.25 µm film was determined to be the most efficient trap.

On-line SFE–SFC has also been described by MacKay and Smith [15]. Four chlorinated organophosphate flame retardants present in polyurethane foams were analyzed. An external calibration with standards injected into SFC was prepared for on-line quantitative extraction. Good recoveries were obtained for all retardants except Amgard V6 from 'Safeguard' due to its low solubility in supercritical CO_2. Oudsema and Poole [16] reported on-line SFE–SFC with formic acid modified CO_2 to determine an organotin stabilizer in a rigid polyvinyl chloride (PVC). A cyanopropyl packed column was used for separation. A solution of formic acid was loaded by syringe into the pump cylinder head to achieve 0.3% (v/v). A cryogenic stainless-steel precolumn was used as a trap.

In our study, efforts have been made to quantify different additives in LDPE using on-line SFE–SFC. In the first part of the study, spiking experiments (on sand) were performed to investigate the influence of different traps and trapping temperatures, injection temperature, extraction pressure, extraction temperature, fluid flow-rate, and extraction time upon extraction efficiencies. The second part of our study involved quantification of the additives from LDPE using the previously determined conditions. Off-line SFE–HPLC and off-line enhanced solvent extraction (ESE)–HPLC were also conducted in the third part of our study in order to compare with results from the on-line SFE–SFC technique.

2. Experimental

2.1. Materials

The following polymer additives were analyzed: butylhydroxytoluene (BHT), butylhydroxyethyl benzene (BHEB), Isonox 129, Irganox 1076 and Irganox 1010.

Additive standard mixtures at various concentrations were prepared using methylene chloride as solvent. An additive standard mixture with a concentration of 5000 ppm for each additive standard was first made and successively diluted to encompass additive concentrations of 100–5000 ppm. Additive standards and the LDPE sample (20 mesh) which originally contained ca. 1000 ppm of each additive were provided by Quantum Chemical (Cincinnati, OH). The samples were approximately 1 year old.

2.2. On-line SFE–SFC

An Isco-Suprex (Lincoln, NE) MPS–225 SFE–SFC consisting of a supercritical fluid extractor, cryogenic collection trap (CC), and supercritical fluid chromatograph was utilized to perform on-line extraction, collection and separation. The SFE–CC–SFC system consisted of a 0.16 ml stainless-steel extraction vessel and a cryogenic collection tube measuring 30×1.0 mm I.D., which had the capabilities of rapid cooling to −50°C and ballistic heating up to 200°C (250°C min^{-1}). A Deltabond (Keystone Scientific, Bellefonte, PA) cyano column,

100×1.0 mm I.D., 5 µm particle size, was used for SFC. SFE–SFC grade CO_2 (Air Products and Chemicals, Allentown, PA) with helium headspace was used as the mobile phase.

The SFE–CC–SFC assembly also included three electronically actuated valves (ten-port, two-position valve; five-port, four-position selector valve; and four-port, two-position injector valve). A schematic diagram of the system is shown in Fig. 1. In the extraction/collection position CO_2 from the syringe pump enters the tee. Tubing from one outlet of the tee leads CO_2 to the injector valve for use only in conventional SFC applications. Tubing from the other outlet of the tee goes through the five-port, four-position selector valve to the extraction vessel. The extracted components carried by CO_2 pass through a linear fused-silica restrictor (50 µm I.D.) to the ten-port, two-position valve, and then into the cryogenic collection trap, which is cooled as low as $-50°C$ with industrial-grade CO_2. All of the extracted materials are then collected in the cryogenic trap, while the expanded CO_2 gas from the cryogenic
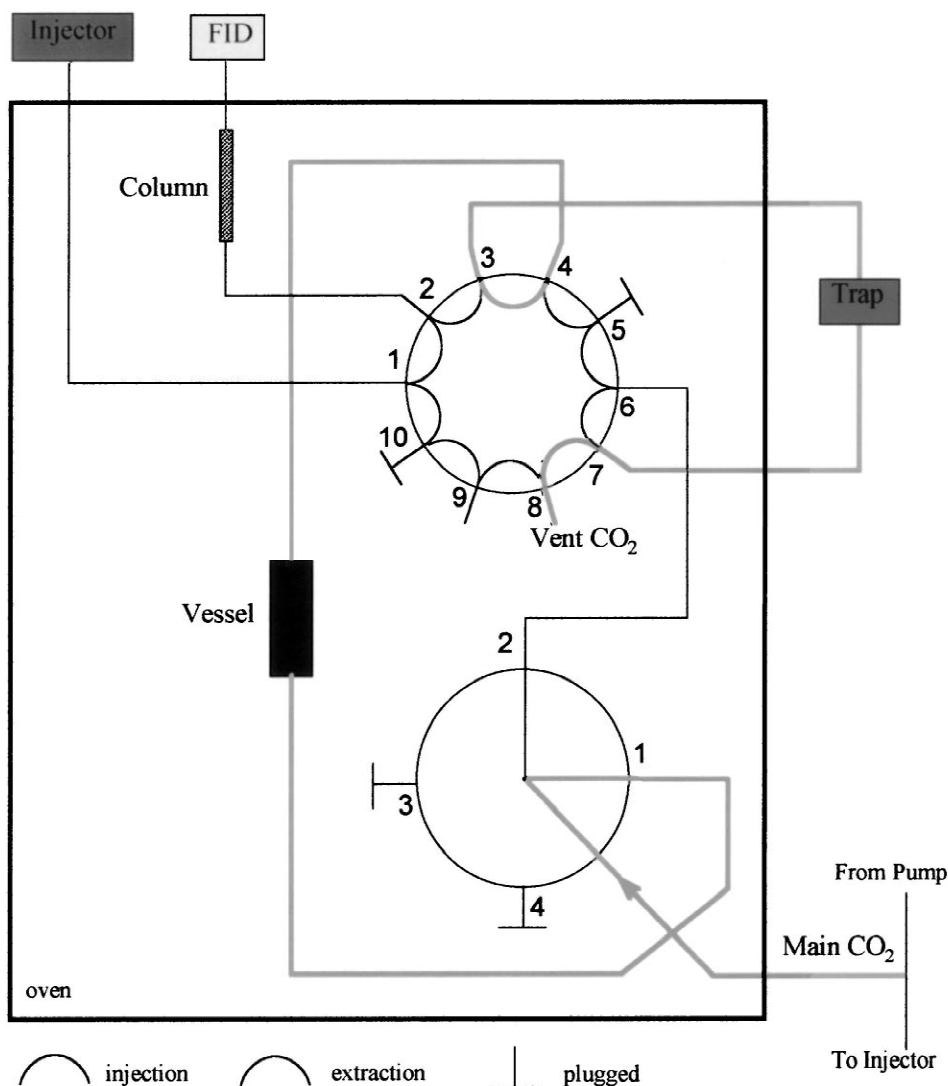

Fig. 1. Schematic diagram of on-line SFE–SFC, extraction/collection mode.

collection trap is vented through the ten-port valve into the atmosphere.

After extraction is completed, the system pump pressure is reduced from the extraction pressure (e.g. 450 atm.) to the starting pressure (e.g. 100 atm.) for chromatography. During this re-equilibration period, the sample remains in the cryogenic collection trap. Upon reaching equilibrium, the ten-port and five-port selector valves are switched simultaneously to the injection/separation mode. In this configuration, CO_2 passes through the tee, the selector valve, and the ten-port valve into the cryogenic trap, which is then ballistically heated to desorption temperature (e.g. 180°C). After backflushing, CO_2 carries the extracted components from the trap back to the ten-port valve and into the packed chromatographic column. The sample passes through a tapered fused-silica restrictor before it reaches the FID, while depressurized CO_2 is vented out the FID to the atmosphere.

2.3. Off-line SFE–HPLC

An Isco-Suprex AP44 automated extraction system equipped with automatic variable restrictor and Accutrap™ collection system was used with the following conditions:

Extraction fluid:	100% CO_2
Oven temperature:	100°C
Pressure:	450 atm.
Restrictor temperature:	75°C
Vessel size:	5 ml
Liquid flow-rate:	1.5 ml min^{-1}
Dynamic extraction time:	30 min
Solid phase trap:	Octadecyl silica (ODS) at 0°C
Trap desorb temperature:	25°C
Trap rinse:	5 ml (50/50) ethylacetate–acetonitrile

The extraction vessel was filled to approximately 80% of its volume with Ottawa sand prior to spiking it with the additive standard. For the LDPE polymer sample, 500 mg of polymer was added onto the sand. A small dead volume was necessary due to expansion of the polymer during extraction.

For the HPLC portion of the analyses, a Hewlett

Packard (Wilmington, DE) series 1050 HPLC was used with the following parameters:

Column:	150×3.9 mm, 5 μm d_p, C_{18}
Column temperature:	50°C
UV detector:	200 nm
Mobile phase:	Gradient from 75/25 (v/v) CH_3CN–H_2O to 100% CH_3CN in 5 min, hold 100% CH_3CN for 14 min, return to 75/25 (v/v) CH_3CN–H_2O for 19.01 min
Flow-rate:	1.5 ml min^{-1}
Sample loop:	10 μl

All solvents were HPLC grade and were obtained from Fisher Scientific (Fair Lawn, NJ).

Quantitation was accomplished by using an external calibration. All experiments were performed in triplicate. The sample size used in off-line SFE–HPLC was much larger (500 mg vs. 2.0 mg) than that in on-line SFE–SFC.

2.4. Off-line ESE–HPLC

An Isco SFX 220 SFE system was modified to conduct ESE. The system consisted of two syringe pumps, an oven, and a 10 ml extraction vessel. A static extraction was performed at 200 atm. and 100°C for 30 min with 10 ml (50/50) ethylacetate–CH_3CN. The extract along with the extraction solvent was collected in a vial, and 10 ml of CO_2 was used to flush the solvent out of the extraction vessel. Post-extraction clean-up was necessary since most of the polymer was dissolved in the extraction solvent. The sample size used for ESE was 500 mg.

3. Results and discussion

3.1. On-line SFE–SFC

One important consideration with on-line SFE–SFC is the impurities in CO_2 which are accumulated in the cryogenic trap. If the level of impurities in CO_2 is too high it may interfere with peaks in the sample chromatogram [17]. In order to eliminate

these interferences, a stainless-steel column measuring 25×2.5 cm I.D. was used as a carbon–alumina purifier before the CO_2 entered the on-line SFE–SFC system. It contained 3/4 activated carbon (4–12 mesh) and 1/4 alumina (80–200 mesh). Another issue with the on-line SFE–SFC system is the so-called 'memory effect', which is defined as the failure to quantitatively remove extracted analytes even after several purges of the system with extraction fluid. The deleterious effect may not present itself immediately, but rather when experimental conditions are changed.

Generally, the success of on-line SFE–SFC greatly depends on the trapping techniques used to recover the extracted analytes from the expanded gas flow after depressurization, particularly when the analytes are volatile. The efficiency of an empty cryogenic trap and a cryogenic trap filled with glass wool was evaluated using the additive standard mixture. Ten μl of the standard solution was loaded in the extraction vessel filled with sand. The solvent was allowed to evaporate for several minutes. Extraction was performed at 450 atm. and 100°C. The trapping temperature was −40°C. The results shown in Fig. 2 clearly indicate that the trapping efficiency

was improved significantly with glass wool in the trap. The empty cryogenic trap could not quantitatively collect the most volatile analytes (e.g. BHT and BHEB). Therefore, the cryogenic trap filled with glass wool was employed in all further experiments.

The effect of trapping temperature on trapping efficiency was next investigated by spiking 10 μl of the 500 ppm additive standard mixture onto the sand. Extraction was performed at 450 atm. and 100°C. The extracts were collected at different trapping temperatures (i.e. −50, −40, −25, −5, 5°C). After 30 min extraction/collection, the SFE–SFC valves were switched to the injection mode and collected materials at 180°C were backflushed to the separation column. As can be seen in Fig. 3, the effect of trapping temperature on the collection of relatively volatile species such as BHT and BHEB was profound. The analytes easily vented out of the trap with the expanded CO_2 at the higher temperatures. On the other hand, no significant difference was found for the collection of Isonox 129, Irganox 1076 and Irganox 1010 at different trap temperatures. Therefore, the cryogenic trap was maintained at −40°C to ensure adequate trapping of this additive package.
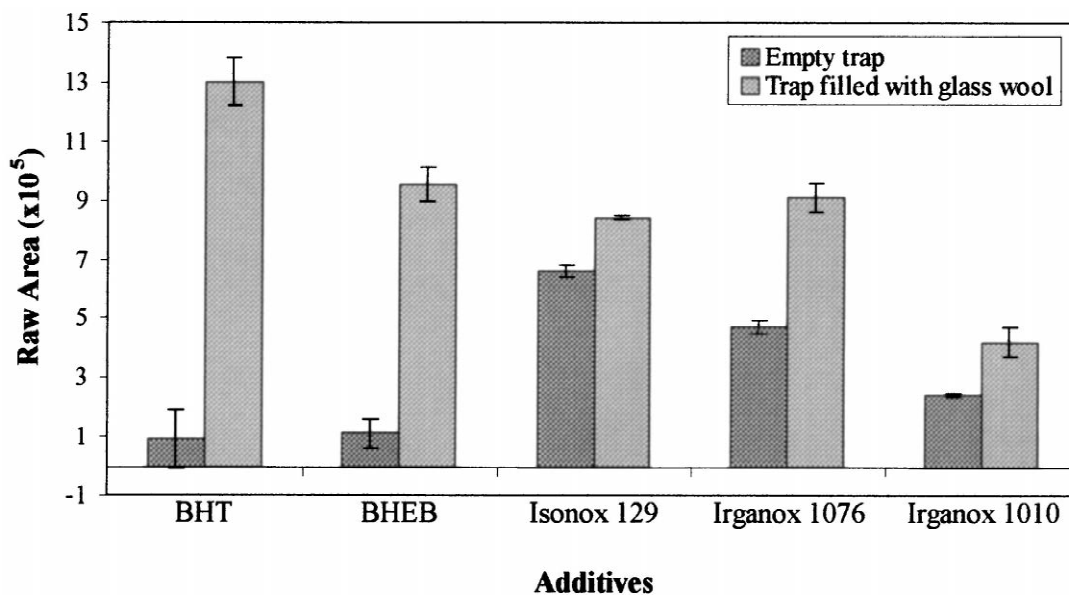

Fig. 2. Comparison of different trapping protocols (spiked sand). SFE conditions: 100% CO_2, 450 atm., 100°C, 30 min, trapping at −40°C. SFC–FID conditions: desorption at 180°C, pressure programming: 100 atm. for 3 min, 100–330 atm. for 7 min, 330–450 atm. for 1.5 min, oven at 100°C, Deltabond™ cyano 100×1.0 mm I.D., 5 μm d_p, FID at 350°C.
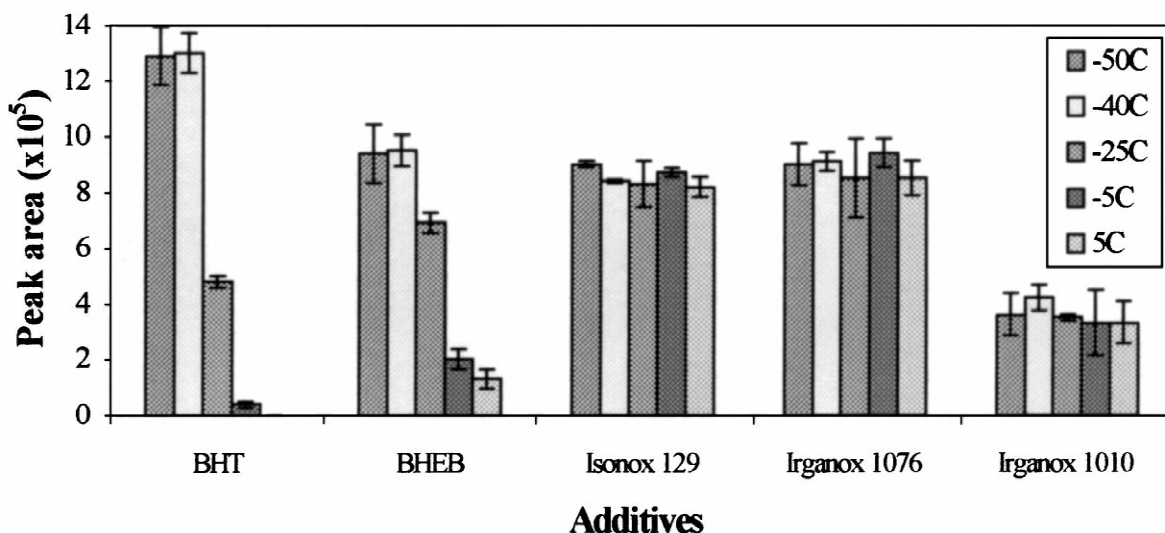
Fig. 3. Effect of different trap temperatures on collection efficiency (spiked sand, glass wool trap). SFE conditions: 450 atm., 100°C, 30 min, flow-rate: 0.65 ml min^{-1}. SFC–FID conditions: desorption at 180°C, pressure programming: 100 atm. for 3 min, 100–330 atm. for 7 min, 330–450 atm. for 1.5 min, oven at 100°C, Deltabond™ cyano, 100×1.0 mm, 5 μm d_p FID at 350°C.

The heating of the cryogenic collection trap prior to SFC was also investigated. After 30 min of collection at −40°C, the system was switched to the SFC injection mode while the cryogenic trap was ballistically heated to 100°C. A second SFC injection was performed with the thermal desorption temperature at 180°C without any additional extraction. By comparing the peak areas, we found even for volatile analytes such as BHT and BHEB, 2–3% of the extracted amount was left in the trap after the first injection at 100°C. The unremoved amounts after the first injection of Isonox 129, Irganox 1076 and Irganox 1010 were 21%, 11% and 9%, respectively. When the injection was first performed at a thermal desorption of 180°C, a following second run showed that no significant amount of analyte was left in the trap.

3.2. Optimization of SFE parameters

The main factors affecting the efficiency of extraction of additives from polymers are the solubility of the additives in the fluid and the rate of mass transfer of the additives out of the polymer matrix [18,19]. In the absence of specific additive–polymer matrix interaction (e.g. sand instead of polymer matrix), the extraction will primarily be controlled by

pressure, temperature, time and fluid flow-rate. The effects of these parameters were investigated by spiking the additive standards onto the sand using the optimized trap conditions. The effect of increased pressure on the extraction of high molecular weight species (i.e. Irganox 1076 and Irganox 1010) was more pronounced than that observed for low molecular weight analytes. The effects of temperature at constant pressure are more complicated than the effect of pressure at constant temperature. Increasing temperature decreases solute–fluid interaction, which results in decreased solvating power. Whereas, at the same time increasing temperature decreases solute–solute interaction, which results in increased solubility. An optimum temperature therefore exists.

One important point must be kept in mind for extraction of real polymer samples. The glass transition temperature (T_g) and melt temperature (T_m) of the polymer sample should be taken into account. The extraction efficiency of a polymer is enhanced above its T_g and is increased still further above the polymer T_m [20]. A temperature above the T_g results in enough molecular motion in the amorphous phase of the polymer so that the SF can diffuse into the region easily. However, a temperature higher than the T_m is not practical because once the crystalline phase melts, clogging the extraction system and

possibly ruining the extraction vessel may easily happen. The LDPE sample used in this work has a T_g well below ambient temperature and its T_m is in the range $106-115°C$. Therefore, the highest temperature practical for this work was below $106°C$.

In the experiments described above, the pre-trap restrictor used was a piece of 25 cm×25 μm fused-silica capillary to afford a liquid fluid flow-rate 0.65 ml min^{-1}. In order to investigate the effect of fluid flow-rate on the extraction efficiency, the restrictor was replaced by a 50 μm fused-silica capillary 25 cm long to obtain a higher fluid flow-rate (i.e. 2.0 ml min^{-1}). A different extraction time was employed for the different fluid flow-rates so that the amount of CO_2 used for each extraction was the same. Faster flow resulted in lower collection efficiency (Fig. 4) because the extracted analytes easily vented out in the form of aerosol with the expanded CO_2 gas flow.

Experiments were also conducted to optimize the extraction time for the additive standards. For this purpose, 10 μl of the additive standard mixture was spiked onto the sand. The extraction was conducted at 450 atm. and 100°C. The liquid CO_2 flow-rate was 0.65 ml min^{-1}. The extracted components were collected at $-40°C$. The extraction of BHT and BHEB was completed in 10 min. There was no

increase in extraction yields of Isonox 129, Irganox 1076 and Irganox 1010 after a total 30 min extraction. In summary, low trap temperature, high extraction pressure, high extraction temperature, and low fluid flow-rate with moderate extraction time resulted in highest extraction efficiency.

Traditionally, there are several standardization techniques employed in the practice of chromatographic analyses: external standards, internal standards and standard addition. External calibration is sensitive to variations in the matrix, and therefore is unsuitable for many matrix systems [21]. Internal standards and standard addition can overcome the matrix effect; however, a homogeneous mixture of standard and sample is difficult to obtain if solid samples are analyzed [22]. To overcome these problems, three point calibration curves of spiked sand with the additive standards were established in the range of 1–3 μg of each additive standard. Ten μl of the standard solution with various concentrations was applied via a microsyringe onto the sand in the extraction vessel. The solvent was evaporated at room temperature before the extraction vessel was pressurized. The extraction was conducted under optimized conditions. Peak area counts vs. the amount of the additive standards was plotted to
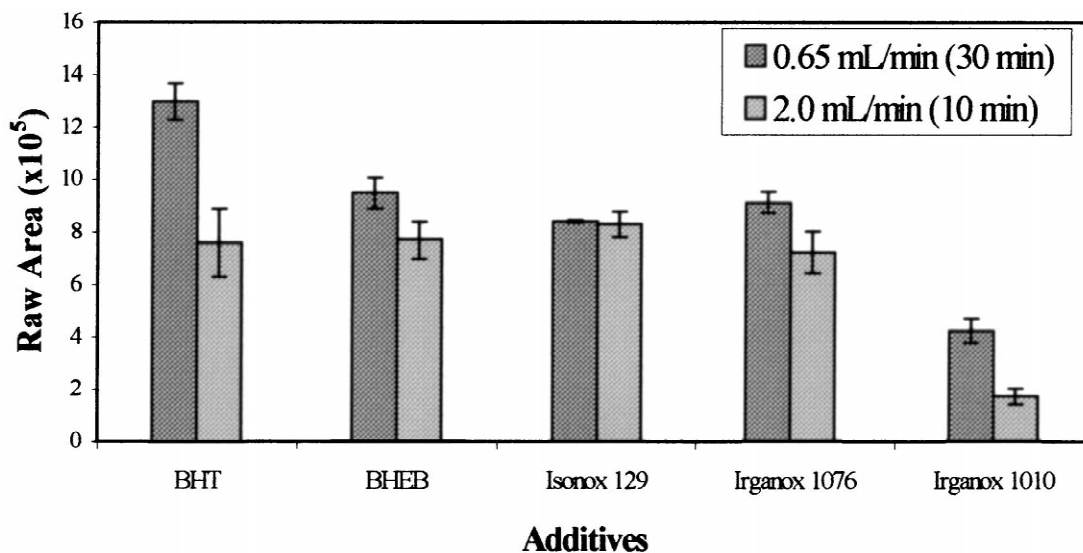

Fig. 4. Effect of liquid flow-rate on collection efficiency (spiked sand). SFE conditions: 450 atm., 100°C, 30 min, trapping at $-40°C$. SFC–FID conditions: desorption at 180°C, pressure programming: 100 atm. for 3 min, 100–330 atm. for 7 min, 330–450 atm. for 1.5 min, oven at 100°C, Deltabond™ cyano, 100×1.0 mm, 5 μm d_p, FID at 350°C.

provide a curve, the slope of which was an area response factor (area counts/μg additive) that could be compared directly to area counts observed in actual polymer samples. Respective correlation coefficients were BHT(0.987), BHEB (0.998), Isonox (0.997), Irganox 1076 (0.998) and Irganox 1010 (0.995).

3.3. Extraction of additives from LDPE sample

The goal of this work was to quantitatively extract additives from LDPE under the previously optimized conditions for spiked sand. The LDPE sample was ground to 20 mesh. In order to make the extracted additive concentration fall into the linear range of the calibration curves that was obtained with spiked sand, approximately 2 mg of the LDPE sample was
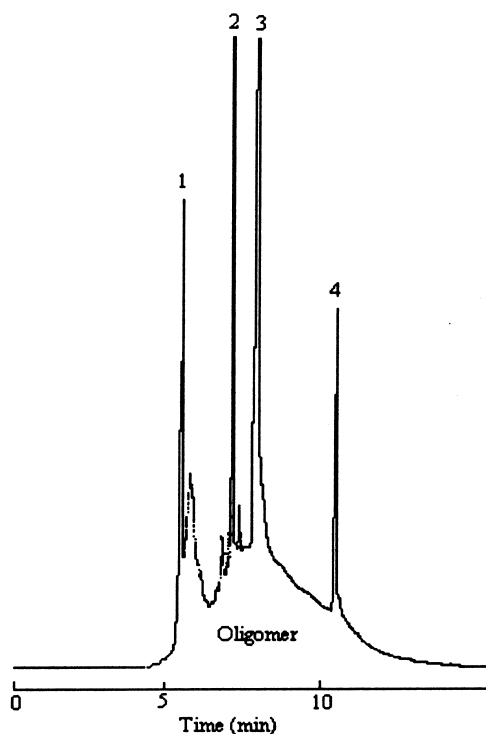

Fig. 5. On-line SFE–SFC–FID chromatogram of LDPE sample (2.0 mg). 1, BHEB; 2, Isonox 129; 3, Irganox 1076; 4, Irganox 1010. SFE conditions: 450 atm., 100°C, 15 min, trapping at −40°C. SFC–FID conditions: desorption at 180°C, pressure programming: 100 atm. for 3 min, 100–330 atm. for 7 min, 330–450 atm. for 1.5 min, oven at 100°C, Deltabond™ cyano, 100×1.0 mm, 5 μm d_p, FID at 350°C.

employed for each extraction. Other reasons for the use of a small sample size were to avoid clogging of the small I.D. fused-silica restrictor, to negate a 'memory effect,' and to avoid overloading the SFC column. Fig. 5 shows a representative on-line SFE–SFC chromatogram of the LDPE sample.

First extraction profiles were obtained for the additives from the LDPE sample using the optimized conditions. It was found (Fig. 6) that the extraction of the relatively volatile and low molecular weight species such as BHEB was exhaustive in 15 min. However, for the extraction of the other three additives, Isonox 129, Irganox 1076 and Irganox 1010, the extraction profile was typical of an analyte that is both solubility and diffusion limited. Our optimized extraction conditions were therefore altered to incorporate a 60-min extraction time.

The percentage recoveries under optimized SFE–SFC conditions of the additives from the LDPE sample are given in Table 1. The mass extracted was obtained by a comparison with the calibration curves for spiked sand. The recoveries were calculated based on the original additive concentration provided by the manufacturer. Only BHEB, Isonox 129, Irganox 1076 and Irganox 1010 were quantified. BHT was not detected most likely due either to the dimerization of BHT which is not extractable [23], the decomposition of BHT, the evaporation of BHT during the grinding process or BHT's concentration was too low for detection. Recoveries greater than 80% for each of the other additives were achieved using the on-line SFE–SFC technique. However, the precision was quite low due to the very small sample size and possibly the inhomogeneous distribution of additives in the polymer product. There could also have been overlap of some of the chromatographic peaks by polymeric interferences. For this reason we next examined off-line SFE–HPLC which readily accommodates larger samples.

A 500 mg sample of the LDPE, approximately 250 times that employed in the on-line SFE–SFC, was subjected to off-line SFE–HPLC. The extracts must be analyzed within 24 h to avoid possible degradation of unstable species. Fig. 7 shows an off-line SFE–HPLC chromatogram of the extract of the LDPE sample. The additive percentage recoveries are also given in Table 1. Lower recoveries were obtained with the *off-line* SFE–HPLC method

Fig. 6. Extraction profile of additives from LDPE sample. SFE conditions: 450 atm., 100°C, 15 min×4, trapping at −40°C. SFC–FID conditions: desorption at 180°C, pressure programming: 100 atm. for 3 min, 100–330 atm. for 7 min, 330–450 atm. for 1.5 min, oven at 100°C, Deltabond™ cyano, 100×1.0 mm, 5 μm d_p, FID at 350°C.
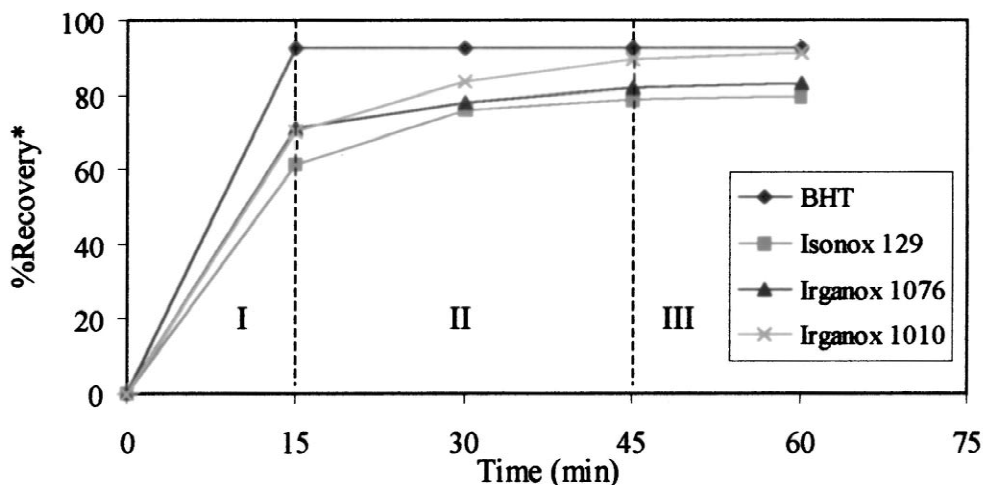
because the coextracted oligomer precipitated from the solid phase trap rinse solution and occluded a significant portion of the analytes. Heating the polymer extract solution would have been helpful to dissolve the oligomer as well as the analytes. However, extreme care would have been essential since some of the additives are thermally unstable. Higher recoveries were, therefore, obtained with the *on-line* SFE–SFC method, most likely due to the fewer number of experimental steps and therefore the reduction in sample handling compared with off-line SFE–HPLC. The precision obtained from the off-line SFE–HPLC was much better compared to that from the on-line SFE–SFC. The different precisions

obtained with the two techniques is believed to arise from the sample size difference (i.e. about 250 times amount of sample employed in off-line SFE–HPLC compared to the on-line SFE–SFC).

Enhanced Solvent Extraction (ESE), also known as Accelerated Solvent Extraction (ASE™), is an extraction method that significantly streamlines (relative to traditional soxhlet) sample preparation with liquid solvents. Solvent is pumped into the extraction cell containing the sample, which is then brought to an elevated temperature and pressure. Minutes later, the extract is transferred from the heated cell to a standard collection vial for clean-up for analysis. The entire extraction process is fully automated and

Table 1
Concentration (ppm) of the additives with one standard deviation from LDPE[a]

	Manufacturer's data	On-line SFE–SFC	Off-line SFE–HPLC	Off-line ESE–HPLC
BHT	875	N.D.	67±1	73±4
BHEB	975	900±160	1020±80	1010±100
Isonox 129	975	780±160	650±7	660±13
Irganox 1076	1000	830±150	490±10	500±15
Irganox 1010	975	900±110	880±40	910±150

[a] On-line SFE–SFC: SFE conditions: 100% CO_2, 450 atm., 100°C, dynamic 60 min, trapping at −40°C, sample: 2.5 mg. Off-line SFE–HPLC: SFE conditions: 100% CO_2, 450 atm., 100°C, dynamic 30 min, ODS trapping at 0°C, rinse with 5 ml ethylacetate–CH_3CN at 25°C, sample: 500 mg. Off-line ESE–HPLC: ESE conditions: 100% CO_2, 200 atm., 100°C, static 30 min, rinse with 10 ml ethylacetate–CH_3CN, flush with 100 ml CO_2, sample: 500 mg. N.D., not detected.
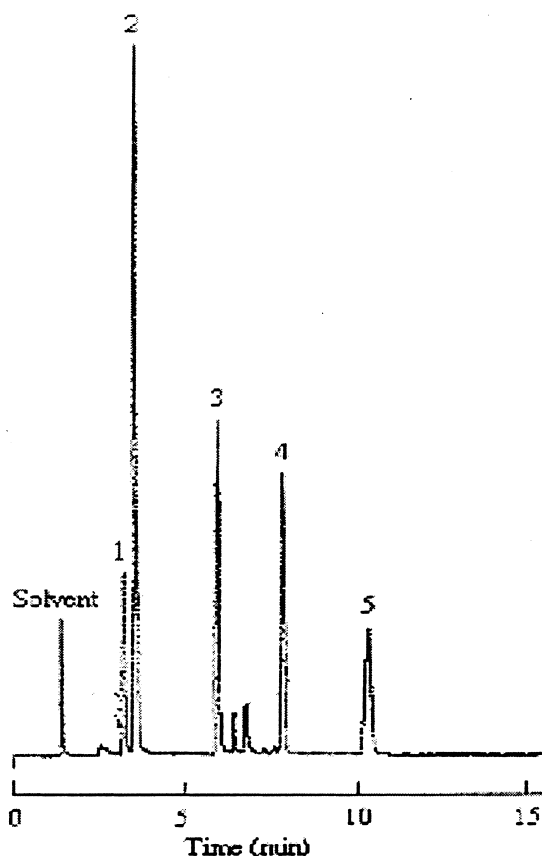
ganox 1010 were comparable using all three methods and each measurement was essentially consistent with the manufacturer's data. Irganox 1076 via on-line SFE–SFC matched the manufacturer's data also, but both methods employing HPLC were quite low. However, in the ESE process, the transfer tubes easily clogged with the messy extracts. Therefore, much clean-up of the system after the extraction was required with ESE as opposed to SFE.

Fig. 7. Off-line SFE–HPLC–UV chromatogram of LDPE sample (500 mg). 1, BHT; 2, BHEB; 3, Isonox 129; 4, Irganox 1010; 5, Irganox 1076. SFE conditions: 100% CO_2, 450 atm., 100°C, 30 min, ODS trapping at 0°C, flow-rate: 1.5 ml min^{-1}, rinse with 5 ml ethylacetate–CH_3CN. HPLC conditions: 150×3.9 mm, 5 μm d_p RP C_{18}, at 50°C, UV detector at 200 nm, mobile phase gradient from 75/25 (v/v) CH_3CN–H_2O to 100% CH_3CN for 5 min, hold 100% CH_3CN for 14 min, return to 75/25 (v/v) CH_3CH–H_2O for 19.01 min.

performed in minutes for fast and easy extraction with low solvent consumption. ESE has been demonstrated to be equivalent to existing extraction methodologies such as Soxhlet and automated Soxhlet for most RCRA (Resource Conservation and Recovery ACT) analytes from solid and semi-solid samples. In our work, a 500 mg sample of LDPE was subjected to off-line ESE–HPLC. Table 1 shows the additive results in concentration (ppm). The measured amount of BHT was exceedingly low via all three analyses. The concentrations of BHEB, Isonox 129 and Ir-

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